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U. S. DEPARTMENT OF AGRICULTURE,
DIVISION OF SOILS.

MILTON WHITNEY, Chief.

SOIL SOLUTIONS:

THEIR NATURE AND FUNCTIONS, AND THE
CLASSIFICATION OF ALKALI LANDS.

BY

FRANK K. CAMERON,
SOIL CHEMIST, DIVISION OF SOILS.

[COOPERATING WITH THE DIVISION OF CHEMISTRY.]

WASHINGTON:
GOVERNMENT PRINTING OFFICE.

1901.

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LETTER OF TRANSMITTAL.

U. S. DEPARTMENT OF AGRICULTURE,

DIVISION OF SOILS,

Washington, D. C., March 20, 1901.

SIR: I have the honor to transmit herewith the manuscript of a technical paper by Dr. Frank K. Cameron, Soil Chemist of this Division, on the nature and function of soil solutions. In accordance with the general policy of the Department, this has been submitted to and has received the indorsement of Dr. H. W. Wiley, Chief Chemist.

I recommend that this paper be published as Bulletin No. 17 of this Division.

Respectfully,

MILTON WHITNEY,

Chief of Division.

Hon. JAMES WILSON,

Secretary of Agriculture.

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SOIL SOLUTIONS: THEIR NATURE AND FUNCTIONS AND THE CLASSIFICATION OF ALKALI SOILS.

By FRANK K. CAMERON.

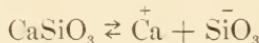
NATURE AND FUNCTION OF SOIL SOLUTIONS.

MUTUAL EFFECT OF ELECTROLYTES.

Soil solutions from which plants draw their food are for the most part aqueous solutions of the mineral components of the soil. Other components, organic generally, are found to a greater or less amount in these solutions, but those substances in the solution, inorganic or organic, which furnish materials for the sustenance of vegetation belong almost entirely to that class of chemical compounds known as electrolytes. It is a characteristic of such compounds that in aqueous solution they impart to the solution the power of conducting the electric current, and from this fact they take their name. This power of conducting electricity when they are dissolved in water is practically confined to those substances known as acids, bases, or salts, which last may be considered as formed by the combination of acids with bases. To one of these three classes may be assigned, almost without exception, all the mineral components and many of the organic components found in soils. A study of the soil, therefore, is a study of a heterogeneous system composed of a number of components, mainly electrolytes, in contact with an aqueous solution of themselves. It is true that the actual amount of some of these components in the solution may be quite small, but to some extent at least every one of the components is dissolved when in contact with the solution. The general considerations involved in such a study have been presented at length in a recent publication of the Division.¹ They can not be given in detail here, but some of the fundamental ideas involved will be repeated, and it will be shown in what manner they can serve to coordinate and explain observations already made upon soil phenomena, and, more important still, how they may indicate many lines of investigation which can not fail to yield a rich harvest both to science as such and to economic husbandry.

¹ Report 64, United States Department of Agriculture.

For purposes of illustration let it be supposed that one of the soil components is calcium silicate (CaSiO_3), and for the moment let the further supposition be made that it does not itself react with water; that is to say, does not form new compounds on going into solution. If this substance come in contact with water some of it will dissolve or diffuse through the water until at length a definite amount of it, depending upon the temperature and the absolute amount of the water, will be taken up and held in solution. The ratio of the amount dissolved to the amount of water is called the solubility and is a constant, characteristic of the substance for a definite temperature. It is now a generally accepted hypothesis that the part of the substance which has gone into solution (called for convenience the *solute*), partially breaks up or separates in the act of dissolving and these separated parts called *ions*, bear definite charges of electricity associated with them in some manner. In the nomenclature of chemistry this fact would be expressed thus:



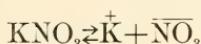
that is to say, that when a state of equilibrium has come about there would be present in the solution some calcium silicate as such and a perfectly definite amount of the ion, calcium, bearing a charge of electricity, positive in sign, and a chemically equivalent amount of the ion SiO_3 , bearing an equal amount of electricity but negative in sign. The solution will of course remain saturated with respect to the undissociated calcium silicate, for enough of the material in the solid phase and in contact with the solution will continue to go into solution until it is saturated with respect to it. This does not imply, however, that the solution is necessarily saturated with respect to any of the possible ions which may be formed.

It is due to the presence of these ions bearing their charges that the solution of an electrolyte will conduct, for if such a solution be made part of a closed circuit there will be a tendency for the positively charged ions to move toward the negative electrode and a corresponding tendency for the negatively charged ions to accumulate at the positively charged pole. At the poles the ions will give up their electric charges, but on losing their charges the ions cease to exist as such, and either reunite to form the undissociated electrolyte, or, more commonly, take part in secondary reactions with the water. The disappearance of the discharged ions disturbs the equilibrium between the undissociated electrolyte and its ions and more of it will dissociate. The process is therefore continuous, and furnishes a vehicle for the transference of electrical energy through the solution.

The extent to which ions will be formed, or, as it is conventionally phrased, the amount of electrolytic dissociation, is a perfectly definite quantity for each individual electrolyte. It is in fact a characteristic constant, but depends upon the concentration and temperature.

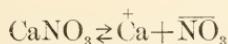
It should be noted that the ions themselves have definite characteristic properties, and these properties may be, and generally are, very different from what they would be if the ions lost their associated or accompanying electrical charges and became merely elements or groups of elements. Further, it has been most amply demonstrated that those chemical properties with which we most commonly have to deal in solutions of electrolytes are those of the ions which the solution may contain. Very much less seldom are we concerned directly with undisassociated portions of the electrolytes. Studies of such solutions become, therefore, mainly studies of solutions of ions.

Suppose another electrolyte, such as potassium nitrate, be dissolved in the solution of calcium silicate under consideration. It will also dissociate partly, thus:



and there will be in the solution undisassociated CaSiO_3 , ions $\overset{+}{\text{Ca}}$, ions $\overline{\text{SiO}}_3$, undisassociated KNO_3 , ions $\overset{+}{\text{K}}$, and ions $\overline{\text{NO}}_3$. But the ions $\overset{+}{\text{Ca}}$ and ions $\overline{\text{NO}}_3$ can and will unite to some extent to form undisassociated $\text{Ca}(\text{NO}_3)_2$ calcium nitrate. In the same manner ions $\overset{+}{\text{K}}$ and ions $\overline{\text{SiO}}_3$ will unite to some extent to form K_2SiO_3 or undisassociated potassium silicate. But the calcium ions and SiO_3 ions withdrawn to form calcium nitrate and potassium silicate respectively will disturb the equilibrium between the undisassociated and dissociated calcium silicate. More of it will dissociate to supply the places of the withdrawn ions, and this will in turn disturb the equilibrium between the dissolved but undisassociated calcium silicate and the substance in contact with the solution, but in the solid phase. More of this latter will dissolve to restore the equilibrium, and in consequence one of the most striking results of the addition of the second electrolyte, which does not furnish an ion in common with those already in the solution, is to increase the solubility of the first electrolyte. It is obvious that just as the presence of the potassium nitrate increases the dissociation of the calcium silicate, just so the calcium silicate causes an increase in the dissociation of the potassium nitrate; that is, they exert a mutual influence on one another and of the same kind.

On the other hand, suppose calcium nitrate to be the second electrolyte introduced into the solution. It would dissociate thus:



and more calcium ions would be added to the solution. But the addition of more calcium ions would disturb the equilibrium between the calcium ions and the dissociated calcium silicate. To restore the equilibrium some of the calcium ions would unite with the SiO_3 ions to form undisassociated calcium silicate, the solution would become supersaturated with respect to this compound, and some of it would in con-

sequence separate in the solid phase and be withdrawn from the solution. In other words, the addition of a second electrolyte which will furnish an ion the same as one of those already in the solution will diminish the solubility of the first electrolyte. Again, it is scarcely necessary to say the reaction between the two electrolytes is mutual in effect.

To summarize briefly, two or more electrolytes brought into solution simultaneously do, and must of necessity, affect one another. If they furnish no ion in common, they increase each other's dissociation (though not necessarily increasing the actual *number of ions* in solution) and consequently their respective solubilities. If, however, a common ion is yielded, the dissociation of the substances from which it comes is decreased, and consequently their respective solubilities are lessened. These effects are in all cases mutual.

It has been stated above that the amount of dissociation, other things—temperature, concentration, etc.—being equal, is a constant for each electrolyte and characteristic of it. It should now be added that different electrolytes vary widely in this respect. Those electrolytes which dissociate very readily, yielding a relatively large number of ions, are called strong and, conversely, those electrolytes which yield only a relatively small proportion of ions are designated weak. In the case of an acid or base the extent to which it dissociates and thus yields chemically active ions is taken as the measure of its strength. This factor of "strength" or dissociating power must be considered in all studies of the mutual effects of one electrolyte upon another, for it is plain that such effects as have been brought out above would be relatively more pronounced with the weaker electrolyte. It does not necessarily follow that the weakest electrolyte would be the first to separate in the solid phase or precipitate from a solution, however, for the absolute solubility of the undissociated salt is a factor, and as to this it is utterly impossible to predicate anything at present beyond empirically determined data. For instance, if ammonium sulphate and calcium nitrate be brought together calcium sulphate will precipitate because undissociated calcium sulphate is less soluble than any other compound that could be formed from the resulting ions. But in so far as it is soluble it is highly dissociated, much more so, for instance, than the very soluble but comparatively weak electrolyte, ammonium nitrate, which would be formed simultaneously with it.

The electrolytes which have been taken for purposes of illustration in the explanations just given are of comparatively simple composition, but exactly the same principles apply to even the most complex silicates or organic compounds, provided they be electrolytes.

It will thus be seen that the soil components have a very decided influence on the solubility of one another, and that a most marked effect may be expected from the artificial addition of another electro-

lyte. From these considerations it is readily apparent that the rôle of a mineral fertilizer is at least twofold. It may furnish plant nutrient itself to the soil solution, but it may have as great an effect in increasing or diminishing the solubility of the original soil components. That this effect may be very great relatively will be seen by citing a few instances.

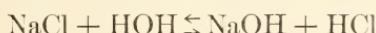
Kippenberger is quoted as having found the solubility of calcium carbonate increased about threefold by the addition of sodium chloride. It has been shown in the laboratory of this Division that the solubility of calcium sulphate in the form of gypsum can be increased about four times by the addition of sodium chloride. The solubility of magnesium carbonate can probably be doubled by the addition of sodium chloride to the solution. Not many quantitative measurements of this kind have been made as yet, but there is very good reason to believe that even more striking increases of solubility of soil components may be brought about by the addition of mineral fertilizers, and investigations along these lines will undoubtedly be of the greatest value to agriculture and to geology as well as to chemistry.

The anomalous results often noted by investigators, that the addition of one plant nutrient to the soil will frequently result in the crop removing unexpectedly large amounts of another nutrient, are readily explained from this point of view, as well as the sometimes detrimental effect of the addition of substances which themselves are known to be harmless.

The electrolytes which form the soil components are mainly silicates, alumino-silicates, aluminates, ferrates, carbonates, etc. They have a marked common characteristic in that they are all salts of weak acids.

HYDROLYSIS.

It is a well-established fact that when an electrolyte dissolves in water a reaction takes place to some extent between the electrolyte and the water, for water is itself an electrolyte, although a very weak one. For instance, sodium chloride will react with water, as thus indicated:



But all of these substances are strong electrolytes and largely dissociated, excepting only the water. The equilibrium constant for water is very low indeed, and the hydroxyl ions from the sodium hydroxide and the hydrogen ions from the hydrochloric acid will reunite to form water, so that the extent to which this reaction will take place is very small indeed—too small to be detected by the usual means at our disposal. That it does take place to some extent, even

with comparatively strong electrolytes, can be readily recognized in some cases. For instance, magnesium chloride reacts with water to form to a small extent magnesium hydroxide and hydrochloric acid, and on evaporating the solution to dryness a very small portion of the volatile hydrochloric acid will be distilled away.¹

By repeating the process a few times the residue will be found decidedly alkaline. In a quite analogous manner, when calcium chloride is thoroughly dehydrated by fusion the residue always contains some little calcium oxide, the hydrolyzed hydrochloric acid having been volatilized.

When the case of an electrolyte consisting of a weak base united to a strong acid, or, vice versa, a strong base united to a weak acid, is considered, this reaction with water, or hydrolysis, becomes much more marked. For example, in the case of nicotine sulphate in aqueous solution it is well known that the solution can not be concentrated by evaporation near the boiling point without serious loss of the nicotine, and this in fact is a serious annoyance in the estimation of this substance. The explanation is quite obvious. The nicotine being a very weak base, its salts are considerably hydrolyzed in the water solution with the formation of free nicotine, which is readily volatilized and distilled off, especially with steam.² On the other hand, the hydrolysis of sodium carbonate, in which a strong base is in combination with a very weak acid, is quite familiar to every one. The alkaline reaction of solutions of calcium or magnesium carbonate is another striking and familiar instance. The efficiency of soap is probably to be explained in a great measure in the same way. Soaps in general consist of organic salts of sodium or potassium, in which strong bases are combined with relatively weak acids, and therefore are more or less hydrolyzed, rendering the base free to act upon the skin or other substance to be washed.

It has been shown by several investigators, notably Clarke,³ W. B. and R. E. Rogers⁴ among others, that a great many minerals dissolve quite rapidly in pure water, although the absolute amount which goes

¹ Mr. Atherton Seidell has verified this statement for me by a careful experiment which yielded very decided results. The solution of magnesium chloride was carried to dryness on the steam bath, taken up with water, and again carried to dryness. After repeating the process some three or four times the solution gave a markedly alkaline reaction with phenolphthalein.

² At my request Mr. Seidell repeatedly evaporated a solution of ammonium sulphate to dryness on the water bath, the residue being again taken up each time with distilled water. After a few repetitions of the process, the solution of the substance, which had originally appeared to be perfectly neutral, gave a decided acid reaction with methyl-orange, Congo red, or litmus. Undoubtedly the weak base ammonium, combined with the strong sulphuric acid, was considerably hydrolyzed and volatilized, even in the presence of an excess of acid.

³ Jour. Am. Chem. Soc., 20, 739 (1898).

⁴ Am. Jour. Arts and Sciences (1848).

into solution is not perhaps very large, and that when the minerals are silicates or alumino-silicates of the alkali bases or alkaline earths the solutions are always decidedly alkaline. Here is presented a very beautiful instance of hydrolysis, depending on the fact that the bases involved—potassium, calcium, etc.—are united to very weak acids, and the resulting solution is in fact a solution in part of the free bases. The amount of base thus set free is of course dependent mainly upon the factors, the amount of the solubility of the undissociated substances, and the strength of the acid compound in the solutions, together with the strength of the particular base involved. The solubility of the undissociated mineral is fortunately seldom of any considerable magnitude. The acid formed by the hydrolysis is usually quite unstable itself and readily breaks down, with the partial separation of the silicon in the solid phase as some form of silica, crystalline or amorphous. The aluminum or iron, etc., which is so frequently a constituent of the acid radical, also yields very insoluble compounds, and is precipitated in such forms that if the solubility of the original mineral was at all considerable it seems probable that the basic constituents would soon be leached away from the surface soils.

This action of water, or hydrolysis, must be a potent factor, not only in making mineral constituents of soils available for plant nutrition, but in the formation of the soils themselves, by breaking down or weathering the rocks from which the soil components are derived. In so far as the addition of other readily soluble electrolytes assist in rendering soluble the mineral components of the soil, as has been indicated above, they may be regarded as assisting in the weathering or ultimate decomposition of these mineral components. It seems worth while to lay stress upon this point of view, for it suggests interesting lines of work for the general geologist, as well as for the soil investigator, and affords a reasonable explanation of many facts hitherto accounted for in a most unsatisfactory manner. For example, it is conventional in the text books to explain the formation of kaolin from feldspar by the action of carbonic acid on the latter mineral. It has been a source of trouble to many students to see how a weak, volatile, and slightly soluble acid like carbonic acid could so readily affect such a stable compound. It is much more reasonable to suppose that in the feldspar there is a very strong base-forming element—potassium—in combination with a very weak acid-forming radical, and that, although but slightly soluble, the compound does dissolve to some extent and is considerably hydrolyzed. The hydrolyzed base, being very soluble, is then readily leached away and by absorption of carbon dioxide forms the carbonate as the result of a secondary or subsequent reaction. The hydrolyzed free acid, being a very unstable compound, breaks down at once, yielding the two very slightly soluble substances, kaolin and silica. Many such illustrations might be cited, but space forbids.

RÔLE OF IRON IN THE SOIL.

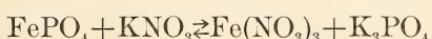
Particularly interesting is the rôle of iron, when studied from this point of view. It is both a weak base-forming element and a weak acid-forming element, and, in consequence, its salts are very readily hydrolyzed. The acid reaction of ferrous sulphate solutions, due to the formation of sulphuric acid by hydrolysis of the salt, is quite familiar to every one. How far we may have to deal with ferrous iron in the soil is still an undetermined matter. It is generally supposed to be of very small importance, but it should be remembered in this connection that there is good reason for supposing that ferrous iron can and does often replace magnesia or lime in certain minerals, and that if these minerals come into contact with the soil solutions there must be some ferrous iron brought into the solution. But ferrous iron, even in the presence of considerable quantities of free acid, is quite rapidly oxidized to the ferric condition, and it is generally supposed that on the surface of the soil grains, where the solution is taking place, the iron has been oxidized to the ferric condition.¹ The salts of ferric iron are as a rule less soluble than the salts of ferrous iron, so that the hydrolyzed ferrous iron is quickly oxidized to ferric hydrates and in this form precipitated, more or less coating and covering the soil grains and protecting them from the further solvent action of the soil solutions. But the ground waters generally carry in solution considerable carbon dioxide, which unites to some extent with the ferric hydrates forming the carbonate or some one or more of the rather indefinite compounds classed under the head of hydrated carbonates. These substances are decidedly more soluble in water, especially when the water is kept saturated with carbon dioxide, whereby they are prevented from decomposing and giving up part of the carbon dioxide contained in them. They are rather unstable compounds, readily breaking down under normal conditions. If by aeration, or in some other manner, the water loses some of its dissolved carbon dioxide, these compounds, being unstable, break down to a greater or less extent and give off some of their carbonic acid, so that the amount of carbon dioxide dissolved as such will be increased and the equilibrium of the system restored. At the same time some of the iron is reprecipitated as the hydrate or hydrate carrying more or less of the carbonate. This process is well exemplified in the case of a well water taken from near Hyattsville, Prince George County, Md., and examined recently in this laboratory. This water when first obtained yielded on analysis 9.44 parts Fe_2O_3 per hundred thousand parts of water, but on standing for twenty-four hours a dense precipitate was formed and an analysis of the filtered water showed but 0.24 part of Fe_2O_3 per hundred thousand. An examina-

¹ This is certainly not the case in some soils, especially in the more arid regions of the West, as a microscopic examination will show.

tion of the precipitate showed it to be composed entirely of hydrate or hydrated carbonate of iron. This water undoubtedly may be regarded as an extreme case, but it is cited here to show that large amounts of iron can be, and probably are, transported in this way. If the process of the separation of the iron compounds be somewhat slow it will precipitate in a more compact or crystalline form. We thus have an explanation of the formation of the sometimes large masses of iron stone, conglomerate, or hardpan which is often found in our fields at various depths, more or less shallow. The iron compound separates from the solution at the particular depth at which it is found because at that point aeration has been sufficient to lower the partial pressure of the carbon dioxide in the atmosphere in contact with the solution, allowing this latter substance to escape, with the simultaneous reprecipitation of the iron compound which cements together the material in which the precipitation takes place. Or it may happen that the solution passes from a fine-textured soil in which the interstitial spaces between the soil grains are very completely filled by the solution, to a coarser-grained soil with larger spaces, which the solution does not completely fill, and into which therefore some of the dissolved carbon dioxide can escape in the gaseous phase. It is interesting to note in this connection that the iron hardpan is frequently found at or near the surface of contact of deposits of markedly different texture.

As interesting and important as are the functions of iron just noted, it should be borne in mind that it is as an acid-forming element that trivalent iron is found in its most stable compounds; and that in all probability an important rôle which it plays in the soil is in the form of ferrates which help to conserve the bases resulting from the decomposition and decay of more complex compounds.

Another function of iron, in which it appears as a base, is worthy of earnest consideration. It is generally held that it plays an important rôle in holding in combination with it the phosphoric acid in the very insoluble compound, iron phosphate. This idea seems entirely reasonable, for, besides the very limited solubility of the substance itself, there is but little assistance to be expected from the hydrolizing effect of water. Both the acid and base are weak, and their corresponding hydrates would be but very little dissociated. Nevertheless, the action of another electrolyte, especially if made up of a strong base and acid, would have a marked effect in increasing its solubility. For instance, let it be supposed that potassium nitrate be added to a soil containing iron phosphates. If the reaction were undisturbed by other influences, then a condition of equilibrium would result which could be represented by the following expression:



But the ferric nitrate would promptly be more or less hydrolyzed,

precipitating ferric hydrate and setting free nitric acid. At the same time the normal potassium phosphate, consisting of a very strong base with a rather weak acid, would also be partially hydrolyzed, forming a secondary or primary phosphate. Probably the hydrolysis would be more extensive in the case of the iron salt, so that the resulting solution would be acid, and this would have to be taken into account in predicting the nature of the alkali phosphates and other substances formed. Nevertheless all these substances would be formed and would exist in the resulting solution, and it would be entirely justifiable to say in this sense that the potassium nitrate had partially converted the insoluble iron phosphate into the readily soluble alkali phosphate, and thus made the phosphoric acid available to the plants. The iron may be justly regarded as of the greatest value in conserving the phosphoric acid, holding it so that it may be taken out gradually, under proper conditions, so that this exceedingly valuable asset in fertility will not be quickly leached out or otherwise removed from the soil. It is not surprising, then, that it has been noted in agricultural practice that the addition of a potassium fertilizer has improved the condition of the soil in regard to phosphates and rendered ambiguous the results of the analyses of the crops.

RÔLE OF CALCIUM IN THE SOIL.

Rather different, however, is the mechanism of the action of lime on the phosphoric acid held by the iron. If the calcium be in the form of a strong electrolyte the action will be analogous to that with potassium nitrate; but if it be added in the form of oxide, hydrate, or carbonate, it is fair to assume, in view of what is known as to the hydrolytic action of water, that to all intents and purposes it will be the hydrate to which attention should be directed. The problem then becomes one of the distribution of the phosphoric acid between the two bases—calcium and iron. The features of the general problem can not be discussed in detail here. A very clear statement of an analogous case will be found elsewhere.¹ It will be sufficient to say that the acid will be distributed between the bases, and that a quantitative expression can be given to the ratio in which the distribution will take place. The problem as it is presented to us is much more difficult than any in which quantitative measurements have actually been made, for the solutions are in contact with the solid phases; furthermore, questions of relative and absolute solubility, for which no accurate data are available, enter into consideration. In general terms, the distribution will take place in favor of the stronger electrolyte.

In the case under consideration the effect of liming may be expected to render the ferric phosphate more soluble by converting a part

¹ Nernst, Theoretical Chemistry (translated by Palmer), p. 432 (1895). See also, Arrhenius, Zeit. für phys. Chem., 5, 1 (1890).

of it into lime phosphate. In a similar manner liming would react with a potash silicate—for example, the acid being distributed between the two bases according to their relative strengths or ionization constants, and the liberated potash becoming, in consequence, more readily available because more soluble. The more or less complete replacement of potash by lime, when added to the soil, has long been known. The problem it presents for study has, however, often been complicated by confusing it with the question of the existence or nonexistence of readily soluble hydrous silicates or zeolites in the soil. Whether or not there be zeolites formed in the soil is really foreign to the problem, for it is evident that if any potassium silicates be in the soil the potash must be released to some extent by the lime.

SOME POSSIBLE FUNCTIONS OF HYDROUS SILICATES.

On the other hand, no satisfactory evidence has been brought forward to show that zeolites or other hydrous silicates may not be formed in the soil beyond the fact that they have not been found there in well-defined crystalline masses. *A priori* one would rather expect that such substances might be formed, for, compared with other silicates they are readily soluble, and the constituent materials are at hand, and, as far as we know, there is no reason to suppose that synthetic processes should not be taking place in the soil, as well as destructive ones. Even if formed only in subsoils or lower depths, the minerals might be expected to be brought into the upper soil layers in solution. Wöhler¹ long since showed that apophyllite could be dissolved in water and recrystallized unchanged from its solution as any ordinary salt. There is good reason to suppose that other minerals of this class would behave in an analogous manner.²

The researches of Tammann³ have shown very conclusively that for some of the zeolites the water they contain is not held as ordinary water of crystallization, but that, as a matter of fact, these minerals are solid solutions in which we may regard the silicates as the solvent and the water as the solute or dissolved substance, and that between certain limits these minerals may dissolve any amount of water, depending, of course, upon the temperature and the partial pressure of the water vapor in the atmosphere in contact with the solid solution. It would seem probable, therefore, that one of the functions of such substances, if they do exist in the soil, is to conserve the moisture, becoming saturated with water, when there is an excess of this agent present, and gradually giving it up in times of drought, so that it can become available to plant growth.

Many investigations have shown that the bases of these hydrous

¹ *Jahresber.*, Liebig und Kopp, p. 1262 (1847-48).

² The Rogers (*loc. cit.*) found this to be the case.

³ *Wied. Ann.* **63**, 16 (1897); *Zeit. anorg. Chem.* **15**, 318 (1897).

silicates are readily replaceable, in part at least, and it has long been believed that the addition of lime to the soil caused a redistribution of the acid radicles of these hydrous silicates, with a consequent separation of a part of the potassium they held in a more soluble form. Recent investigations of Clarke and Steiger,¹ which show that at comparatively high temperatures the bases in these minerals may be partially replaced by ammonium, also indicate that the replacement may go on more slowly or to a lesser extent at ordinary temperatures.

But, further, the very beautiful investigations of Friedel² showed that just as these minerals could take up water, in precisely the same way they could take up ammonia. In fact, the water, at that time supposed to be water of crystallization, could be partly replaced by ammonia, so that it seems quite probable that another function of these compounds is to conserve ammonia in the soil.

It is true that the ideas just advanced must be regarded as speculative, but they are presented here as showing that the long-existing controversy as to the existence of zeolites or other hydrous silicates in the soil has a real importance, both scientific and economic.

ACIDITY OF SOILS.

From what has been said above the impression might be obtained that soil solutions would generally be alkaline, since the acids are nearly all weak, often unstable, breaking down with the separation of insoluble products, and the bases to which they are combined are strong. But, as a matter of fact, we know that soils are for the most part somewhat acid in character. It should be remembered, however, that soil solutions may generally be regarded as culture solutions for various organisms, which feed upon and break down the complicated organic matters contained in the soil, an almost invariable accompaniment of these processes being the formation of acids, sometimes organic, sometimes mineral, as in the case of the nitrifying organisms. The purely oxidation processes taking place in the organic matter must further yield considerable amounts of organic acid. The excretions from plant roots, which are, in the main, acid, are generally supposed to be important factors in this regard. These acids, of course, serve, in part, to neutralize the bases.

RÔLE OF CARBON DIOXIDE.

A very important rôle in this respect is, in all probability, played by carbonic acid or carbon dioxide dissolved in the solutions. Carbon dioxide is formed in the soil through many agencies, and the amount there present must often be very considerable. Generally speaking,

¹ Am. Journ. Sci., **8** (158), 245 (1899); **9**, 117 (1900).

² Bul. Soc. Min., **19**, 94 (1896).

it is always present in relatively much greater amounts than is to be expected from a consideration of its small partial pressure in the atmosphere above the soil.

It has been shown in the laboratory of this Division that solutions of carbonates in contact with ordinary atmospheric air always absorb some carbon dioxide, and for a given temperature and total concentration there is a definite, constant ratio between the amounts of carbonate and bicarbonate at equilibrium. Except possibly at very low temperature, or at very great dilutions, there is always a considerable amount of normal carbonates present. The equilibrium can be displaced toward the formation of more bicarbonates if the partial pressure of the carbon dioxide in the vapor above the solution be increased—that is, in effect, by dissolving more carbonic acid in the solution. But, as has been just said, these conditions obtain in the soil, since there is generally an excess of carbon dioxide in them. Mr. Briggs has recently shown that even dry soils show a remarkable power to absorb this agent from the atmosphere, and, together with the quantities being constantly formed in the soil, yield far more than enough to convert the carbonates to neutral bicarbonates and render the soil weakly acid. It is not to be supposed that this implies the necessary existence in the soil at any given time of considerable quantities of bicarbonates, for these substances are all fairly soluble and comparatively readily leached out, as witness the fact that the soils derived from the decomposition of limestones are nearly always deficient in lime. Great differences exist in this respect, however, as is brought out very clearly in contrasting the behavior of calcium bicarbonate and magnesium bicarbonate. The researches of Treadwell and Reuter¹ indicate that calcium hydrogen carbonate, or the bicarbonate, is a fairly stable compound, and can even exist as such in solution when the partial pressure of the carbon dioxide above the solution is quite low. Being also fairly soluble, the calcium in this form of combination is quite readily leached away. Magnesium hydrogen carbonate, on the other hand, is exceedingly unstable, and can only exist as such in the presence of large amounts of free carbon dioxide. In consequence it very readily inverts to the less soluble normal carbonate, and is less readily removed from soils by leaching. This subject is now being investigated experimentally in the laboratory of this Division.

The effect of dissolved carbon dioxide itself, or the resulting carbonic acid, has long been the subject of controversy and the evidence presented by various investigators is very conflicting. That a considerable amount of ionic hydrogen must be present in a solution saturated with respect to carbon dioxide would lead, according to

¹ Zeit. für Anorg. Chem., 17, 170 (1898).

investigations of Kahlenberg and True¹ and of Heald,² to the notion that such a solution must be toxic to plants. Kearney, in the laboratory of this Division, has shown that this is certainly not true in some cases. Further, the ground solutions must often contain very large amounts of carbon dioxide, even when plants are growing in a most satisfactory manner. The subject obviously requires more careful investigation.

SUPPOSED POISONOUS ACTION OF HEAVY METALS.

It has long been noted that salts of the heavy metals in general have a strongly toxic effect on plants. Many investigations, for instance, have been made with the salts of iron and of copper, and it is generally believed that these metals have been definitely proved to be most harmful when dissolved, even in quite small amounts. While it can not be said that these conclusions are in themselves wrong, it would seem that they may in many cases be open to criticism, in view of the methods used in their investigation. It should be remembered that these metals are quite weak bases as compared with the acids to which they are united, and their salts on going into solution must and will be considerably hydrolyzed with the formation of some small amounts of free acid. The researches of Kahlenberg and of True³ have shown that the toxic effect of the hydrogen ion is relatively very great indeed, a concentration of about one reacting weight of any strong acid per 6.400 liters of aqueous solution being sufficient to cause the death of plants. So that it is a question worth serious consideration as to whether or not the supposed toxic action of the metals was not in fact due to the hydrolyzed acid formed when the metallic salts were brought into the culture solutions.

SOIL ANALYSES.

To obtain a method of analysis which would give a true indication of the mineral constituents of the soil available for plant nurture has long been the subject of investigation. It was early recognized that the ultimate analysis of the soil would not furnish the data desired, for questions of solubility, etc., entered into the problem, and it was obvious that a distinction must be made between the *available* plant food and the total amount of the constituents which go to make up the food which might be present in the soil. Various solvents have been tried and the attempt made to correlate the amounts thus extracted from the soil with that taken from the soil by various crops. Not only have various acids been tried, but solutions of various concentrations. The

¹ Kahlenberg and True, Bot. Gaz., **22**, 81 (1896); Kahlenberg and Austin, Jour. Phys. Chem., **4**, 553 (1900), True, Am. Jour. Sci. (4) **9**, 187 (1900).

² Bot. Gaz., **22**, 136 (1896);

³ Loc. cit.

difficulties presented have been found to be very great, for it is obvious that the nature of the action of strong mineral acids must be quite different from the weak acids normally present in the soil during plant growth. This has led in recent years to two notable series of investigations. Dyer has attempted to prepare a solution which would more closely simulate the acid solution about the roots or root hairs of plants. It is obvious that the acids excreted by root systems will not come in contact with all the particles of the soil, but only with the contiguous ones, at least in its first concentration; that the acidity of these secretions from different plants in different degrees of maturity or of different species might well be expected to differ widely; that the time factor must enter very largely on account of the slow rate of solution of these slightly soluble soil components. It has been claimed for his method that the amount of the principal mineral foods extracted, i. e., potash, lime, phosphoric acid, bears a strikingly constant relation to the well known cropping value of lands, certainly for the Rothamstead soils. Whether or not it will hold for other soils is open to doubt, evidence pro and con having been brought forward. But as a matter of fact, it does not appear that any material advantage has been shown by this method, for exactly the same claim has been made for hydrochloric acid extractions—that the amount of plant food dissolved is a *factor* of that available.

Maxwell, in a series of ingenious papers, has proposed a method involving the digestion of soils with dilute solutions of aspartic acid. His reasoning is quite different in some respects from Dyer's, but in the main the two methods are closely analogous. While it may be admitted that the aspartic acid solution does extract plant food from the Hawaiian soils in proportions comparable to the amounts truly available, it does not follow that it will answer as well for other soils; and, moreover, the objection still holds that no advantage over the hydrochloric acid digestion is really gained by its use for what it is claimed to show is a probable factor of the available plant food.¹

The question then becomes pertinent why any solvent would not do as well, for instance, sodium chloride. The answer is that the advantage in using an acid is mainly an analytical one; the excess of acid, mineral or organic, can be gotten rid of readily, leaving no awkward residue to interfere with the determinations of the materials extracted from the soil. Moreover, from the point of view of the electrolytic dissociation hypothesis acids present a decided advantage, in that one of the ions resulting is hydrogen, not a common ion with any furnished by the mineral electrolytes in the soil. Therefore the solvent action of acids

¹Dr. Wiley informs me that the results of an extended investigation in his laboratory indicate that an analysis of the material extracted from a soil by digestion with a hundredth normal solution of hydrochloric acid gives a much closer approximation to the effect of a growing crop than any scheme yet proposed. The results of this investigation will shortly be published.

might be expected to be much greater than that of the corresponding salts, which fact is borne out by experience. The strong mineral acids would of course have the greater solvent action in comparison with the weak organic acids.

From the facts just presented it would seem that the various other methods do not present any real advantages over digestion with hydrochloric acid, while digestion with the latter reagent presents distinct analytical advantages. It does not seem worth while to displace it, therefore, until another method which does present distinct advantages has been proposed. That such a method may be devised is earnestly to be hoped, but it must come from a consideration of all the factors involved in the problem and can scarcely be expected to result from purely empirical work. A thorough study of these factors must necessarily be a precedent for intelligent attempts along this line.

ABSORPTION BY SOILS.

Another peculiarity of soils must be considered. It has been well established that solutions, when passed through mixtures of finely divided material, undergo radical changes. The filtering out of colored materials not mechanically held but actually dissolved, by means of charcoal or "bone black," is a familiar case. The great difficulty experienced by all analysts in washing certain soluble salts from precipitates or filter paper is another illustration of this property. It has been clearly shown that in general any solid surface in contact with a solution causes a tendency to manifest itself in the dissolved substances to concentrate in a very thin layer of the solution next the solid surfaces. That this effect is very limited is evident; otherwise our solutions in vessels of ordinary size would not approximate the condition of perfectly homogeneous mixtures. That it might be of immense importance, however, in capillary spaces is very probable. What the effect of the nature of the surface of the solid in contact with the solution may be has received but scant attention so far, other than in the case of the growth of crystals in contact with their own solutions, or as to the area of surface exposed. But the nature of the substances dissolved, and especially when the substance is an electrolyte, is known to be a most important factor. That some salts can be readily washed through a soil, while others will remain in the most persistent way, is well known. That a considerable difference exists in the way in which various salts will be brought to the surface by capillary movements of the soil solution has been established. Thus the soils may be said to show a selective absorption or ad-sorption, as the phenomenon is now generally known. It must be candidly confessed that this phenomenon is not at all well understood. Comparatively little study has been given to it in the past. It is now the sub-

ject of investigation by Mr. Briggs in the laboratory of this Division, and much interesting information and data in this connection will soon be available. Another way in which the soil shows a selective absorption must be noted. It was early observed by Liebig, Way, and other investigators that if a solution of an ammonium salt be passed through a soil the ammonium radical was very largely retained by the soil. In the case of ammonium chloride, for example, a weak base is combined with a very strong acid and some hydrolysis is to be expected. The question might at once be asked, Why does the ammonium hydrate remain behind and let the acid residue be washed out when the ammonium hydrate is as soluble or more soluble than the acid? It might in turn be answered that the soil does, in fact, show a decided selective absorption toward ammonium hydrate, as shown by the experience of Liebig and Way when passing solutions of ammonia through soils. This may be due in part to a replacement of other bases by ammonium in the silicates of the soil, the stronger bases being taken out by the stronger acids or by other possible chemical reactions, of which several readily suggest themselves. It is well to bear in mind that the alkali bases and ammonia solutions, although the substances are very soluble, do show a marked tendency to remain on solid surfaces. The difficulty with which they are washed from the hand, for example, is very striking, and it would seem that it is probably due to a saponifying action on the grease. That organic matter of this general description is present to some extent on soil grains and may hold back in part the hydrolyzed ammonia seems not improbable. It is hoped that some experimental data bearing on this view will be available soon.

Quite recently an investigation by Oehsner de Conick¹ has been published, of which some of the experimental results are interesting in this connection. It would seem that when solutions of salts of some of the heavy metals are passed through animal charcoal a selective absorption is apparent. For example, in the case of a solution of ferric chloride practically all the iron was retained in the charcoal, the acid going through. This salt, it should be observed, is one which hydrolyzes very readily, yielding the very slightly soluble ferric hydrate as one product. It is quite conceivable that on coming in contact with the large surface afforded by the animal charcoal, either through adsorption or otherwise, concentration changes take place in the solution, followed by hydrolysis, the precipitation of the insoluble iron hydrate, and the ready leaching of the very soluble hydrochloric acid. Similar phenomena, differing only in degree, might be expected in the case of soils being the filtering media. Further study along these lines would undoubtedly yield results of great practical importance as well as of scientific interest.

¹ Compt. rend., 180, 1627 (1900).

RÔLE OF ORGANIC MATTER.

The organic matter of the soil merits some attention here. It is a complicated subject, no doubt, and no attempt to treat it exhaustively is contemplated at this time. Whether it be the accumulations of many decaying vegetations from the growth of successive years, as in the case of virgin soils, or whether it be formed partly from decaying vegetation and partly from the addition of organic manures, this material contains plant food originally taken from the soil and in the process of decay returned to its original source.

Besides returning the mineral constituents to the soil, and in general in a form readily assimilable by crops, the ultimate decay of the organic matter would be expected to yield carbon dioxide, water, and nitric acid. These substances are undoubtedly found, but as the result of direct oxidation, of microorganisms, enzymes, etc., many intermediary substances are formed. In many cases they are not at all well understood. It seems to be accepted by many that the principal products thus produced are acids or amido acids of the aliphatic series. These substances, while generally subject to further decomposition through the action of microorganisms, ferments, etc., nevertheless play their part in the soil meanwhile as weak electrolytes, as has been pointed out in discussing the acid reaction common to most soils.

SUMMARY.

It is believed that the views presented above, while themselves speculative in some respects, together with the facts brought out, justify the following general conclusions:

(1) The mineral, and to a large extent the organic, components of the soil are electrolytes, and soil solutions are mainly solutions of electrolytes.

(2) The hypotheses of electrolytic dissociation and hydrolysis in aqueous solution give rational explanations for many phenomena hitherto regarded as inexplicable or exceedingly obscure.

(3) The rational procedure in the chemical investigation of the soil, from the point of view of its relation to crop culture, is to study the soil solution and in what manner it is modified by contact with the solid and gaseous components of the soil.

CLASSIFICATION OF ALKALI SOILS.

FORMATION OF ALKALI.

In order to obtain an intelligent appreciation of the practical problems presented by the accumulation of alkali in the soil, a clear idea as to its formation and accumulation is necessary. By "alkali" is meant any accumulation of water-soluble inorganic material sufficient in

amount to have a deterrent effect on vegetation. This amount varies quite widely, however, depending as to its lower limits among other things upon the nature of the plants which go to make up the vegetation. Such accumulations are characteristic of arid regions, owing to the fact that there is not sufficient rainfall to leach from the soils the more soluble materials resulting from the decay and weathering of the rocks and more complex soil components. This process is sufficiently well known and understood to render further explanation at this time unnecessary. It is not generally recognized that true alkali conditions may and occasionally do occur in humid regions and are in their general features strictly analogous to those of the arid regions. Some details as to this point will be given later.

It is not proposed to discuss here why or how alkali comes to be present in a soil or soil crust, but it will be desirable to describe certain general changes, physical and chemical, which it undergoes after accumulating in any given area. These changes are brought about mainly through the agency of water.

In general all the components which go to make up the alkali in any particular case are present in the soil in some form or other before the application of water, although sometimes salts which materially affect the character of the alkali of an area may actually be brought in by irrigating waters.

The various salts composing the alkali vary greatly in solubility. The more soluble salts will naturally go into solution more readily and rapidly than the less soluble ones. It will be convenient to consider the various phases of alkali presented to our attention as the results of the action of aqueous solutions of certain soluble salts upon less soluble salts. In general the substances which form the alkali of arid regions consist of either chlorides, sulphates or carbonates of sodium, potassium, calcium, and magnesium, or mixtures of two or more of these salts. Other components occasionally enter, as nitrates, phosphates, or salts of barium, strontium, etc., but these may safely be considered as unusual or at least as relatively unimportant.

Alkali has been conveniently classified as white and black. The white alkali, although in appearance it may not be and frequently is not white in color, is that form in which no sodium nor potassium carbonates appear as ingredients; the black alkali is that form in which sodium carbonate is an essential ingredient and by its solvent action on organic matter often gives a dark color to the mass, although very frequently it is found in quite a white condition. This classification has been a very useful one in the past and is yet in some ways a convenient one, although it is often very unsatisfactory. For many purposes a classification based more specifically upon the chemical characteristics of the alkali or system of salts present would be preferable. That such classification can readily be made it is hoped will

become evident as this paper proceeds. It may be said at once that while the data and analyses of other investigators have been considered and weighed, the material accumulated in the studies of this Division has naturally had a paramount influence in forming the views here expressed.

METHODS OF ANALYSIS.

While the methods now in use in the investigations of the Division of Soils present many unique features, none of them seem to call for special comment at this point except the chemical analyses. These need a few words of explanation, as they present certain radically different features from the analyses obtained by the methods of other investigators. In consequence, no fair comparison of the results from different sources can be made without at least allowing for the differences in the methods employed. This subject has already been commented upon in a former paper from this Division,¹ and a detailed description of the methods adopted in this Division will shortly be given in another publication.

It may be frankly admitted that it has not as yet been possible to devise any scheme which will give positive and direct knowledge as to the composition of the ground solutions as they actually exist in the soil; nor does there appear to be any prospect of the early realization of this important and much desired object. The relations of the various solutes or substances in solution are largely dependent upon the absolute concentration of the solution, absorptive power of the soil grains, and other factors about which we as yet know very little indeed. It has been necessary, therefore, to adopt an arbitrary method.

It is the practice in this laboratory to stir 50 grams of the soil or crust into a liter of distilled water and then allow the suspended material to settle for twenty-four hours. Five hundred cubic centimeters or more of the supernatant liquid is then decanted through a folded filter and the various determinations made upon 100 cubic centimeter portions of the filtered solution, which are taken to represent the soluble portions of a 5-gram sample of the original soil or crust. Of course in some cases the concentration of solution thus obtained is not the most favorable for the analytical work to be done, in which case it is modified accordingly either by taking a larger sample and concentrating the filtered solution or by diluting to a convenient amount a definite portion of the filtered solution; but for the sake of uniformity all leachings of the original soil or crust samples are made in the proportion of 1 gram of sample to 20 cubic centimeters of water. The only other feature worthy of comment is the method used for determining the amounts of carbonates, bicarbonates, and chlorides present. These three components are determined in one aliquot portion of the

¹ Report No. 64. United States Department of Agriculture, 1900.

solution, according to the method described in former publications of this Division.

It is of course obvious that the relative proportions of carbonates and bicarbonates thus found in the soil leachings are not those which will exist in the soil itself. The distilled water used in the laboratory is often very rich in dissolved carbon dioxide, and the amount so dissolved is a varying quantity. It will disturb the distribution of the bases between the carbonic ($-CO_3$) acid and hydrogen carbonic or bicarbonic ($-HCO_3$) acid. This distribution is dependent upon the absolute concentration and temperature. Still other factors enter, as the partial pressure of the carbon dioxide in the atmosphere above the solution. This factor is unquestionably much modified in transit from the field to the laboratory. It does not seem advisable to simply state both carbonates and bicarbonates as carbonates alone, because totally misleading conclusions are often indicated by this procedure. It is our practice, therefore, to state the bicarbonates as well as the carbonates as actually determined, and, when the ratio of these components is desired, to supplement the laboratory determination by one made in the field at the time the sample is collected. In the case of water sent in for examination the amounts of carbonates and bicarbonates found are always stated as such, but only in exceptional cases is the dissolved but uncombined carbon dioxide determined.

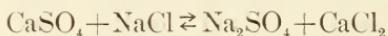
The actual determination of the carbonic acid and hydrogen carbonic acid as such in all solutions examined serves another useful purpose in that by determining all the acid and basic radicals which may be present in the solution, and then balancing them as salts, it is possible to check the accuracy of the analytical work. This is a matter of great importance when, as is frequently the case, a large number of analyses must be made in a limited time, and the making of duplicates for each analysis is quite out of the question under the exigencies of the work.

The statement of the analytical results is now made in terms of the possible ions which may be formed in the solution. For the present it is proposed to continue the statement in the form of combinations as salts, as a concession to those workers who have not become accustomed to the more rational form; but it can not be insisted too strongly that this method is inherently wrong and may be misleading. The particular way in which the data are combined is, in the vast majority of cases, a purely arbitrary matter. It is perfectly certain that the salts as thus stated never exist in the solution in the amounts indicated. In fact, there is every reason to believe that all the possible combinations which the various ions can form are present to some extent. It would, therefore, seem much better and safer to abandon this arbitrary method of stating and considering analyses, except under special conditions, and to become accustomed to the consideration of the possible ions which might be formed.

PECOS TYPE.

From a general inspection of the analyses of the water-soluble constituents of the soils and crusts of the alkali areas, together with a study of the conditions in the field, it would appear that the nature of the alkali in any particular area has predominating features which may be considered as characterizing and differentiating it from other alkalies. In the Pecos Valley it has been made very evident that the predominating feature is the contact of waters carrying considerable quantities of sodium chloride, with the gypsum found abundantly in the soil, the gypsum, in fact, being in some places the main component of the soil. As has been pointed out above, the sodium chloride was also in the soil in the solid phase before the advent of the water, which may, in its initial condition, when applied to the land, have been quite pure. On the other hand, the water frequently does carry much matter (mainly sodium chloride) in solution long before it reaches the area under consideration. The sodium chloride, being so much more soluble, will be taken up long before the gypsum is appreciably affected, and we are therefore justified in regarding this problem as the action of water solutions of sodium chloride upon gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or the dihydrate of calcium sulphate.

In aqueous solutions a reaction takes place between gypsum and sodium chloride which may be represented thus:



part of the calcium and sulphions of the sparingly soluble calcium sulphate being converted into calcium chloride and sodium sulphate, compounds much more soluble than gypsum. If the solution were saturated with respect to gypsum, by being kept in contact with this substance, more of the gypsum in the solid phase would go into solution to restore the equilibrium between the solid gypsum and its solution, which had been disturbed by the withdrawal of some of its component parts or ions to form sodium sulphate and calcium chloride. In other words, the gypsum becomes more soluble on account of the presence of sodium chloride and the solution more concentrated with respect to the total salts dissolved.

By the movement of the solution through the capillary spaces of the soil and the evaporation of the water at the surface the salts are brought toward the surface of the soil. If the solution becomes saturated before it reaches the surface, separation of solid salts will take place, but in any case the tendency will be toward the formation of a crust of the dissolved salts on the surface of the soil as they separate from solution on the evaporation of the water. The various salts on separating are more or less well crystallized, with the exception of the calcium chloride, which, on account of its great hydroscopicity, is dehydrated only under extreme conditions and probably never

separates in well-defined crystals in the field. It is evident that if water be added to the crust the rate at which the several components will redissolve is dependent not only on their respective solubilities but also very largely on their physical states, whether in large, well-defined crystals, exposing a relatively small surface to the solvent action of the water, or in a fine, pulverulent condition, thus exposing a very large surface to the action of the solution, etc. The calcium chloride would evidently go into solution more quickly than any other component of the crust. If the water were allowed to stand in contact with the crust for a sufficient length of time all the salts would dissolve, to a greater or less extent, until a state of equilibrium was reached; but this is not what takes place when water is added, either by irrigation or by rain. It has been pointed out by Mr. Thomas H. Means that the downward movement of such waters in the soil is quite rapid and is through the larger soil spaces, in contradistinction to the slow, upward movement of these waters through the capillary soil spaces; consequently on the addition of water to the soil or crust the calcium chloride, which goes into solution so much more rapidly than the other salts, is rapidly leached out and carried far down into the lower depths of the soil. When evaporation again sets in at the surface the calcium chloride, which has been carried so far below the other salts, either fails to reach the surface altogether or does so in lessened amounts. Thus it is that we practically never find calcium chloride and sodium sulphate in the crust in equivalent amounts, as we should expect *a priori* on the basis of the reaction between sodium chloride and calcium sulphate with the formation of some calcium chloride and an equivalent amount of sodium sulphates.

So far in this discussion it has been tacitly assumed that the rate of movement of the different salts in the capillary spaces of the soil, *after they have gone into solution*, is the same for all salts. Some investigations by Mr. Briggs indicate that this assumption is probably correct, in spite of the long-held opinion that marked differences exist; but even if there be different rates for the different salts, it is incredible that the differences could be of such magnitude as to affect materially those features of the phenomena which have just been considered.

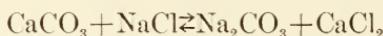
The calcium chloride which has been washed down into the subsoil accumulates there in certain places, and then on prolonged drought is sometimes brought to the surface in very large amounts in spots of limited area. On account of its well-known and very great property of deliquescence it keeps the surface where it has accumulated quite damp, even during periods of protracted drought. This gives a darker appearance to the soil where the calcium chloride has accumulated than that of the surrounding drier areas where this salt has not accumulated, these darkened areas being locally known in the Pecos Valley

as black alkali spots, although chemical examination shows them to be quite free from soluble carbonates.

The metathesis or interaction of calcium sulphate and sodium chloride is the predominating feature of the alkali in the Pecos Valley. It is modified to some extent by the presence of other salts, as the salts of magnesium, for example; but these latter are always present in much smaller quantities than are the calcium and sodium salts. Soluble carbonates are almost entirely absent and merit no attention in this area. Since the Pecos area was the first of the gypsum-sodium chloride type to receive extended investigation by this Division, it has seemed appropriate to give its name to this type of alkali. It is therefore proposed, tentatively at least, to classify areas in which the interaction of gypsum and sodium chloride is the predominating feature under the heading, Pecos type.

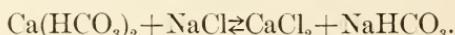
FRESNO TYPE.

It has become evident that in the area about Fresno the prevailing feature of the alkali problem from the chemical point of view is the contact of aqueous solutions of sodium chloride with calcium carbonate. Large quantities of calcium carbonate are found in the soils of this area. Frequently it is the cementing material for more or less extensive beds of hardpan at various depths, usually a few feet below the surface and generally parallel to it. The sodium chloride in solution on being brought into contact with calcium carbonate reacts at once as thus indicated:



calcium chloride being formed, as in the Pecos type, but sodium carbonate being the other constituent instead of sodium sulphate as in the area last considered. The same general considerations apply here. The salts are brought to the surface by evaporation of the solvent and the movement of the solution through the capillary spaces of the soil. They are then, on the addition of water at the surface, partially dissolved and carried quickly down, the calcium chloride being more rapidly removed than the other salts during the process.

The study of this type presents some specially interesting phenomena. As has been pointed out elsewhere, the action between the calcium carbonate and the sodium chloride is much facilitated by the presence of carbon dioxide, this substance reacting with the calcium carbonate to form the much more soluble bicarbonate or hydrogen carbonate and this latter substance then reacting with the sodium chloride. The reaction then would be expressed thus:



The sodium hydrogen carbonate thus formed would be brought to the surface and in much greater amounts than if the normal calcium

carbonate had been its origin. On desiccation, the sodium hydrogen carbonate would be very largely inverted to the normal carbonate. Probably in the field the effect of carbonic acid just described is always considerable, for Mr. Briggs has shown that soil grains have the power of condensing very considerable quantities of carbon dioxide, the soil thus containing much more of this agent than one would suppose from its very small partial pressure in the atmosphere above the soil. Moreover, wet or dry areas containing much organic matter are, from the nature of the case, especially adapted to the formation and retention of carbon dioxide. In such areas the production of black alkali is notoriously great. It is very probable, as has been pointed out in another place, that practically only calcium hydrogen carbonate or the bicarbonate is to be considered in soil solutions in contact with solid calcium carbonate.

The presence of magnesium carbonate with the calcium carbonate, as is frequently the case in soils of this class, introduces some modifications as to degree in the formation of soluble carbonate; for magnesium carbonate is more soluble than calcium carbonate, and therefore its active mass would be greater. Magnesium hydrogen carbonate is less stable than the corresponding calcium salt, but more soluble; and magnesium readily forms basic carbonates in concentrated solution, which are very alkaline. Therefore the contact of this substance with sodium chloride would be expected to yield soluble carbonates more readily and in much greater amount than would the calcium carbonate alone. These views are fully substantiated by the investigation of certain alkali soils from California containing much lime-magnesium carbonate.

The occurrence of calcium chloride spots is quite common in this area. Usually there is also a small amount of soluble carbonates or bicarbonates present. When the calcium chloride is large in amount, the amount of soluble carbonate is quite small, and not infrequently disappears altogether; for calcium carbonate, being quite insoluble as compared with the other salts present, and likewise being but little dissociated, would be formed and precipitated as such. In such spots the application of water to the surface will first wash the excessive amount of calcium chloride away, and then the calcium carbonate will in turn react with the sodium chloride to re-form sodium carbonate. The formation of small amounts of black alkali may well be expected as one of the first results of irrigating such spots. With good drainage, however, the evil would be but a temporary one.

In areas of this type are occasionally found small deposits of nitrates. This is to be expected, for here the nitrifying organism finds lime carbonate to neutralize the excess of nitric acid formed, and its functions are thus not interfered with and kept down to a low limit by an accumulation of its own product.

Since Fresno is the first area in which these relations have been carefully studied and in which they are not disguised to any considerable extent by the presence of other salts, it is proposed to designate alkali areas of the calcium carbonate-sodium chloride class as belonging to the Fresno type.

SALT LAKE TYPE.

The type of alkali most commonly met is one in which the conditions observed may be regarded as the result of the action of aqueous solutions of sodium chloride upon calcium carbonate (or calcium hydrogen carbonate) and gypsum simultaneously. By the action of the sodium chloride upon the calcium carbonate some sodium carbonate would be formed, and also an equivalent amount of calcium chloride. By the action of the sodium chloride upon the gypsum sodium sulphate would be formed, and again an equivalent amount of calcium chloride. This second reaction would take place in the direction of the formation of calcium chloride to a greater extent than the first, for the sulphates are stronger electrolytes than the carbonates, and, moreover, the solubility of the gypsum is probably in most cases greater than the solubility of the lime carbonate, even though there be much carbon dioxide present. The formation of the common product, calcium chloride, would tend to retard both reactions in the direction of the formation of this substance, but more the one involving the calcium carbonate. The formation of the corresponding sodium carbonate is therefore very much lessened by the presence of the gypsum, a fact which has long been known empirically and which has been sometimes employed in the amelioration of the conditions in land containing black alkali by the addition of gypsum or land plaster. The reaction between the gypsum and the calcium carbonate would simply result in lowering the solubility of both salts, because they yield a common ion, but the effect would be much more marked in the case of the carbonate, both on account of its being a weak electrolyte and of its lesser solubility. Therefore the amount of the lime carbonate in the solution, or its "active mass," is much lessened with a corresponding lessening of the extent to which it can react with the sodium chloride to form sodium carbonate.

It must be remembered that the rôle of carbon dioxide is probably of great importance in this connection. The amount of this substance in the soil atmosphere may be quite large, and in consequence the solubility of the lime carbonate may be considerably increased by the formation of the hydrogen carbonate. This might well increase somewhat the amount of sodium carbonate formed and at the same time lessen to some slight extent the formation of sodium sulphate. This is a matter of great importance, for it indicates that in this mixed type of alkali some soluble carbonates are to be expected, although the amount will be small and may usually be neglected in an economic

consideration of the area involved; but in the case of the application of gypsum for the correction of black alkali, the relative proportion of gypsum applied, to the salts already present is small. It may be expected to fulfill its rôle temporarily by acting on the soluble carbonates in immediate contact with it; but an increase of the soluble carbonates, by more of this material coming to the surface from lower depths or by its formation from an increased solubility of the lime carbonate through an increase in the carbon dioxide dissolved in the ground solutions, will require further additions of land plaster. Therefore this method of ameliorating black alkali can be regarded as but a temporary expedient, and has the further disadvantage that the action of the sodium chloride upon the gypsum results in an increase of the soluble salts in the soil. On the other hand, the presence of a large proportion of soluble lime salts has the apparent effect of enabling plants to withstand much larger quantities of other salts than would be possible in the absence of calcium from the soil solutions.

The characteristics of this type of alkali are, then, the presence of soluble chlorides, sulphates, and the relatively small but varying amounts of soluble carbonates.¹ The first area containing this type of alkali that received detailed attention from this Division was in the Salt Lake Valley, Utah. The type is therefore tentatively designated as Salt Lake type.

MODIFIED TYPES.

At Tempe, Ariz., it appears that the original conditions are very similar to those at Fresno, Cal., in that the principal reaction involved is the one between sodium chloride and calcium carbonate. But the investigations of Professor Forbes, of the Arizona Experiment Station, and of Mr. Means, of this Division, have shown that considerable amounts of soluble sulphates are constantly being added to the soils through the application of irrigating waters carrying rather large amounts of these substances in solution. The result is to gradually modify the original type of alkali, making it more nearly resemble the Salt Lake type, although the amount of lime sulphate formed in the soil is hardly sufficient to justify a reclassification under this latter heading. The area is rather to be regarded for the present as a modification of the Fresno type.

In the virgin soils of this area, or in those very recently brought under irrigation, the formation of soluble carbonates has frequently been noticed; but in those soils which have been irrigated for some time with the sulphate-carrying waters the occurrence of soluble carbonates in more than traces, or practically negligible amounts, has been found to be unusual. These observations are entirely in accord with the ideas developed above.

¹See analyses, p. 111, Report 64, Field Operations of the Division of Soils, 1899, U. S. Department of Agriculture.

In the valley of the Sevier River, Utah, the alkali areas are of unusual interest, the alkali being essentially of the Fresno type. The soils are uniformly underlaid by sandy formations, giving good natural underdrainage, and hardpan areas are, therefore, unusual. Even in the virgin soils the amounts of alkali are never very large, and in the irrigated areas, as might be expected with good under-drainage, the amounts of alkali are considerably diminished.

It has been found by Mr. Gardner, of this Division, that in the virgin soils of this area there are considerable amounts of soluble normal carbonates, but as the total amounts of soluble salts decrease in the soils the carbonates decrease also, the proportion of hydrogen carbonates to normal carbonates greatly increasing. This is in entire accord with the laboratory observations of Cameron and Briggs¹ on the equilibrium between carbonates and bicarbonates in aqueous solution. A direct comparison between the field observations and those of the laboratory is not always possible, for the conditions in the laboratory study involved contact of the solution with ordinary atmospheric air, containing a very small amount of carbon dioxide, while the soil solutions in many cases must have been in contact with an atmosphere containing many times the amount of carbon dioxide to be found in ordinary air. In a general way, however, the agreement between the two sets of observations is very satisfactory. It was found that seepage waters fresh from these soils contained, as a rule, no normal carbonates, although always containing some hydrogen carbonates. If these waters be allowed to stand in contact with air for a while, either in pools or by running in the river courses or canals, so that they more nearly approach equilibrium with the air, there is always a partial inversion of the hydrogen carbonate to normal carbonates, as evidenced by the reaction of the solutions toward phenolphthalein.

These observations have an important bearing on alkali studies, as they show most clearly that not only is underdrainage of great importance in diminishing the actual amount of alkali in the soil, but that where there is black alkali this much dreaded substance is at the same time very largely changed to the much less noxious hydrogen carbonate. The change becomes the more nearly complete as the total amount of soluble material decreases.

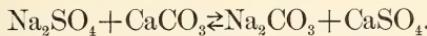
BILLINGS TYPE.

In the valley of the Yellowstone, in Montana, a distinctly different type of alkali is found.² There the alkali consists almost entirely of

¹ A description of this work will appear at an early date in another publication of this Division.

² The Alkali Soils of the Yellowstone Valley. By Milton Whitney and Thomas H. Means, Bul. 14, Division of Soils, U. S. Department of Agriculture, 1898.

sulphates, only traces of chlorides being found. While soluble carbonates occur, as has been amply demonstrated in the laboratory of this Division by examinations of crusts collected near Billings, they are always in very small amounts, which can practically be disregarded in a consideration of the problems presented by this area. Crystals of gypsum are abundant in the Yellowstone soils and in the rocks from which these soils are formed. Occasionally the gypsum is associated with relatively small calcium carbonate deposits. Sodium or magnesium sulphate, the most common of the soluble salts of this area, would decrease the solubility of gypsum because they furnish a common ion in the SO_4 group. They would react to some extent with calcium carbonate, making it more soluble, according to the following scheme:



From the well-known properties of the individual salts, it could be prophesied, what is actually found to be the case, that equilibrium in this system is reached when the reaction is mainly from right to left. In other words, the solubility of calcium carbonate is but slightly increased in the presence of sodium sulphate. In the presence of carbon dioxide, and the consequent formation of calcium bicarbonate or hydrogen carbonate, the reaction is much further displaced to the right, as indicated by the above scheme. On desiccation at the surface the sodium hydrogen carbonate would mainly invert to the form of the normal carbonate, and in the presence of so much gypsum and magnesium sulphate as is always present in these soils it would be quite rapidly converted to the slightly soluble alkaline earth carbonates and sodium sulphate.

Practically the only salt to be considered in this area is sodium sulphate and possibly in some cases magnesium sulphate. It would appear that the Pierre shales, from which a large portion of the soils of this valley are derived, contain considerable quantities of sulphide of iron as marcasite or pyrites. On weathering this material is superficially oxidized to the very soluble ferrous sulphate. By further oxidation and hydrolysis the major part of the iron is precipitated as the very slightly soluble ferric hydrate, this substance then becoming more or less mixed with carbonate of iron by absorption of carbon dioxide.

Hydrated carbonate of iron has been identified in some of the samples from this locality now in the collection of the Division. At the same time that the ferric hydrate was precipitated free sulphuric acid must have been formed. This acid was quickly neutralized by its action upon the other mineral components of the soil, especially lime carbonate. It would seem probable that this process is in large part responsible for the sulphates so abundant here.

LIMITATIONS OF THE CLASSIFICATION.

The classification here proposed seems expedient at the present stage of the studies of this Division upon alkali problems. It is desirable to have a nomenclature which will go further than the division of alkali into black and white, respectively, and which will include as much as possible of those ideas now held to be involved in the processes taking place in the material systems (solutions) which have been considered above. Whether or not the form it is given here will prove well advised time and usage will determine. Some, at least, of its shortcomings are obvious enough now. Other types than those described above may have to be added, and this in itself may ultimately prove a very weak point, although for the present the classification be justified. The basis of the classification is professedly a chemical one alone. Other considerations, such as the physical or mechanical composition, texture of the soil, etc., may and probably will at some time have to be incorporated and an entirely different set of types then selected. At the present stage of our studies, however, this does not seem to be essential or even desirable. It is believed that the formulation of our ideas in the description of the types here given will lend light to the handling of the problems involved and the classification itself will be found useful and sufficient for some time to come. That modifications must come with further work is one of the most interesting and cheerful features to investigators in this line, for it is a most positive indication that there is much yet to be learned and that the ground is clearing for further progress in this most important field.

SUMMARY.

The views presented in this paper may be summarized as follows:

(1) A classification as black alkali or white alkali, depending upon the presence or absence of sodium carbonate, is inadequate in view of our present knowledge of alkali phenomena. A more comprehensive classification is desirable. Such a classification appears to be possible on chemical grounds, considering alkali conditions as the result of the action of aqueous solutions of certain soluble salts upon less soluble salts.

(2) The action of sodium chloride solutions upon gypsum is the predominating feature in certain areas and seems to be well typified by the conditions in the valley of the Pecos in New Mexico. The solubility of the gypsum is apparently much increased by the presence of the sodium chloride due to the formation of the soluble salts, sodium sulphate and calcium chloride. In such an area practically the only salts which will have to be considered in the ground solutions are sodium chloride and sodium sulphate as well as calcium sulphate. Calcium chloride is sometimes found concentrated to a considerable extent, but usually in localized and generally small spots. Owing to its keeping

the soils of these spots moister and, therefore, darker than the surrounding soils, such spots are locally known as black alkali spots.

(3) The action of solutions of sodium chloride upon calcium carbonate is the predominating feature of some areas. The region about Fresno, Cal., seems to furnish a good illustration of this class. As a result there is always found a greater or less formation of sodium carbonate, the soluble and very noxious component of black alkali, and the very soluble calcium chloride. Such regions are generally further characterized by the presence of a hardpan at a distance of a few feet below the surface and generally parallel to it, the cementing material of which is calcium carbonate. In such areas there is a tendency toward an accumulation of the soluble carbonates at the surface of the soil. Calcium chloride accumulations, in spots of comparatively restricted area, are frequent accompaniments and are often mistaken for bad black alkali spots, although the presence of soluble carbonates in more than very small quantities is an impossibility.

(4) The class of alkali most commonly encountered is that in which the predominating feature is the simultaneous action of solutions of sodium chloride upon gypsum and calcium carbonate. In such an area the formation of soluble carbonates can take place to only a very limited, generally negligible, extent. The apparent increase in the solubility of the gypsum is also much less than when the calcium carbonate is not present. The alkali of the Salt Lake Valley appears to be a good illustration of this type.

(5) Much less frequently other types of alkali are encountered, as at Billings, Mont., where the soluble material in the soils appears to be almost entirely sulphates.

(6) Modifications of the types described above are more or less frequently found. They may possibly be of such importance as to warrant a separate classification, as, for example, the conditions found to exist in the valley of the Sevier, Utah.

(7) The classification here proposed is believed to be comprehensive and is founded on scientific principles. It is elastic and will readily admit of modifications. Principles other than those now recognized in it may be introduced without the accompaniment of radical changes. It can be made as specific as the advance of our knowledge from time to time will justify.

(8) In conclusion it must be reiterated that the specific classes outlined above are suggested tentatively and rather as illustrating the principles involved than as final definitions. It is proper that the delimitation of the various classes should be made by those who come in actual contact with the phenomena in their field studies. The purpose of this paper will be accomplished if it furnishes a starting point for the gradual development of a comprehensive, scientific, conventional classification of alkali conditions.

OCCASIONAL OCCURRENCE OF ALKALI IN HUMID REGIONS.

CASE IN MARYLAND.

Early in May, 1900, while on a visit to the Maryland Experiment Station at College Park, Md., Professor Whitney observed a dark stain or crust alongside the dirt roadway running through one of the fields of the station's grounds. A small sample was brought to the laboratory of this Division, and on examination gave such remarkable results as to make a more thorough examination seem desirable. On request, Prof. W. T. L. Taliaferro, of the Maryland Agricultural College, kindly collected a sample for us. It consisted of a dark brown-colored crust taken from the surface of the soil to a depth of one-eighth of an inch. It was carefully separated from the soil beneath with a sharp-cutting chisel. The sample was taken from various spots on the dirt road as it crossed the field and outside the wheel tracks. The road had been made by scraping with a road machine the soil from the neighboring fields and throwing it in the center, being subsequently shaped. The road material, therefore, might be expected to be the same as the soil of the contiguous field, but so far as we have been able to learn nothing like the crust we have examined has been observed on the surface of the field itself. That it should be sought for is obvious from the results we obtained, and it is hoped that systematic observations in this direction will be made in the near future.

Fifty grams of the air-dried material were stirred into a liter of water. The mixture was thoroughly agitated from time to time and then allowed to settle for twenty-four hours. The supernatant liquid was decanted through a filter, and analyses¹ of the water soluble constituents made on 100 cubic centimeter portions. The results follow:

Total solids soluble in water, 1.83 per cent, composed as thus indicated :

NO_3	Cl	SO_4	Ca	Mg	Na	K
69.00	4.82	1.31	15.66	3.40	3.40	2.41

Combined in the conventional manner the results give:

CaSO_4	CaCl_2	$\text{Ca}(\text{NO}_3)_2$	$\text{Mg}(\text{NO}_3)_2$	NaNO_3	KNO_3
1.86	7.55	51.20	20.68	12.47	6.24

It thus appears that this crust contains nearly 2 per cent of readily water-soluble salts, more than enough to characterize the soil as an "alkali" soil if it had been found in the arid regions. It would certainly prohibit the growth of any of our ordinary crops if it extended to any considerable depth in the soil and with this concentration. The origin of this material is not evident, for we are informed that these

¹ Made by Mr. Seidell, of this Division.

fields had not been fertilized, at least recently, and certainly with no such large amounts as these analyses would indicate. We have, then, as far as can be seen, no special conditions to account for this phenomenon, and it follows that "alkali" conditions can occur even in humid regions. The idea suggests itself that possibly this phenomenon may occur much more frequently than has been suspected hitherto, and that it would be well in the future to look for its occurrence in humid areas and closely observe the accompanying conditions as to weather, climate, soil, moisture, etc.

From the figures given it will be observed that about 50 per cent of the soluble material was calcium nitrate, and that about 90 per cent was in the form of nitrates. In this respect this crust differs from those usually found in arid areas of the United States. Nitrates are found occasionally by our field parties and of course they can and do occur in large deposits, as in the well-known Chilean deposits, but the usual salts with which we have to deal in the arid regions of this country are chlorides, sulphates, and carbonates. These facts, while indicating probably material differences in the origin of these readily soluble salts, are not so important at the present stage of our studies as that they can and will accumulate in the surface soil to the serious detriment of the plants, and that the phenomenon as observed here in the humid East is closely analogous to its appearance in the arid West. Therefore it should be sought for during periods of severe drought, even when these periods be of comparatively short duration.

The water solution was examined for phosphates, but if present they were in such small quantities as to make their determination impracticable. Mr. F. P. Veitch of this Division has found that with strong hydrochloric acid he was able to extract about 0.1 per cent phosphoric acid (expressed as P_2O_5) from this crust, while his researches on the type formation to which this soil belongs shows but 0.035 per cent P_2O_5 or about one-third as much as this crust contained. It would seem, therefore, that even the more moderately soluble constituents show a tendency to accumulate in the surface crust as well as the most soluble constituents of the soil waters. It will be noticed that the crust was found on ground which had been rolled down smoothly and compactly, presenting a surface from which evaporation would take place much more readily than from the surface of loose earth in the contiguous fields. It was this rapid evaporation from the surface, undoubtedly, which occasioned the accumulation of the soluble material there.

CASE IN FLORIDA.

In January, 1898, while working near Starke, Bradford County, Fla., Professor Whitney collected a specimen of a peculiar-looking crust which he observed along the edge of a path in a pine woods. An

examination of this material was made by Mr. Thomas H. Means, of this Division. Twenty-five grams of the material was thoroughly shaken with 500 cubic centimeters of water.

The material which had been thoroughly air dried or dried in the oven was very differently wetted. The soil grains appeared to be covered with an oily or greasy substance. The solution which was obtained was very dark in color and decidedly acid. About 0.70 per cent of the soil was found to have dissolved, of which 0.51 per cent was organic matter, leaving about 0.19 per cent of the soluble mineral matter. It was shown that practically the only base present was sodium, bare traces only of calcium, potassium, and iron being found. The acid present in greatest amount was shown to be hydrochloric acid. Sulphuric acid was also found and, strange to say, a considerable amount of phosphoric acid. This crust was decidedly different in composition, at least from the Maryland crust described above. It was more like the crusts found in some arid regions, in that it contained such a relatively large amount of sodium chloride. The rather large amount of phosphoric acid present is certainly not characteristic of the alkali crusts of arid regions, but is occasionally observed. The chief distinctions between the crust under discussion and those of the arid regions are the very large amount of organic material present, unusual in arid regions except in the presence of much alkaline carbonates, and the fact that the Florida crust contained but the one base, sodium, while the crusts of the arid regions contain usually calcium, magnesium, and potassium salts, as well as those of sodium. In the case of this Florida crust it will be observed that, like the case of the Maryland crust, it was found on a compacted smooth surface, from which evaporation was much more rapid than from the surface of the surrounding soils.

REPORTED OCCURRENCES FROM VARIOUS LOCALITIES.

Mr. Clarence W. Dorsey reports having observed the accumulation of water-soluble material at the surface in spots in fields at Biers post-office, near Cumberland, Md. The accumulation is sufficient after a spell of dry weather to kill the vegetation and to attract cattle as to a salt lick.

Similar accumulation appearing on the surface after more or less prolonged dry spells has been reported from Mississippi and Louisiana. In these cases it was concluded at the time the phenomena was observed that the soluble material was mainly sodium chloride, but precise data are wanting. Near Durant, Holmes County, Miss., there are spots reported¹ to be from a quarter to a half acre in extent, on which nothing will grow. If a seed germinates, it dies soon after

¹ Samples 3919 and 3920, Division of Soils, U. S. Department of Agriculture.

it is up. The presence of sodium chloride has been shown. The spots remain as bare as a floor.

Another example,¹ a soil collected about 10 miles north of Houston, Tex., contained 0.37 per cent of sodium chloride in April, 1899. Other examples from this area might easily be quoted.

The presence of iron sulphides in the soil or subsoil frequently occasions the presence of soluble sulphates on the surface during "spells of dry weather." By surface oxidation the iron sulphide is converted to the soluble ferrous sulphate. This salt is readily hydrolyzed in part, forming free sulphuric acid, which in turn forms soluble sulphates by action on the soil components. The soluble sulphates are brought to the surface by the capillary movements of the soil waters, and in dry weather are frequently deposited as a coating or crust on the soil. An interesting case of this kind occurring near Washington has been described by Merrill.² Mr. Bonsteel has called attention to a similar occurrence on the shores of Lake Cayuga in New York. Many such instances could undoubtedly be found.

From the foregoing descriptions it is evident that the essential differences between conditions obtaining in the soils of humid and arid regions are rather those of degree than of kind; that the fundamental forces at work are in reality the same, and that the study of the phenomena presented in one area can and should be of the greatest value in interpreting those of another area.

¹ Sample 4002, Division of Soils, U. S. Department of Agriculture.

² Proceedings National Museum, Vol. XVII, p. 87 (1894).



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